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京都大学	博士（工学）	氏名	陶 然 (TAO, RAN)
論文題目	Synthesis and Application of Fullerene Bis-Adduct Isomers as Novel Electron Acceptors in Polymer Solar Cells (ポリマー太陽電池新規電子アクセプターを目指したフラーレン二付加異性体の合成と応用)		
<p>（論文内容の要旨）</p> <p>This thesis aims at high-efficiency polymer solar cells via the synthesis and application of fullerene bis-adduct isomers as novel electron acceptors.</p> <p>The first is a brief introduction of polymer solar cells (PSCs) and the recent research progress on the photovoltaic materials to improve the device performance. Different strategies to increase open circuit voltage (V_{OC}) of PSCs via molecular engineering of fullerenes are elaborated, among which fullerene bis-adducts are a family of the most promising acceptor materials for PSCs due to their high-lying LUMO energy levels. However, fullerene bis-adducts are involved with the problem of regioisomers which disturb the molecular packing of fullerenes in the bulk heterojunction (BHJ) structure and decrease short circuit current (J_{SC}) of PSCs. To enhance V_{OC} and J_{SC} simultaneously, a new methodology of utilizing the pure isomer of fullerene bis-adducts as the acceptor for PSCs is proposed.</p> <p>In Chapter I, a series of alkoxycarbonyl-substituted dihydronaphthyl-based [60]fullerene bis-adduct derivatives (denoted as C2BA, C4BA and C6BA with the alkyl chain of ethyl, <i>n</i>-butyl and <i>n</i>-hexyl, respectively) are synthesized to investigate the effects of alkyl chain length and substituent pattern of fullerene bis-adducts on the film structures and photovoltaic properties of bulk heterojunction PSCs. These fullerene bis-adducts are obtained through Diels-Alder reaction in moderate yields. The regioisomers of the C4BA products are isolated by preparative HPLC and subjected to comparative study with those of the C6BA products, while the isomers of C2BA are unable to be separated due to a lower solubility. A shorter alkyl chain length causes lower solubility of the fullerene bis-adducts (C6BA>C4BA>C2BA), thereby resulting in the increased separation difficulty of respective bis-adduct isomers. On the other hand, optical and electrochemical properties of these fullerene bis-adducts are unaffected by the alkyl chain length of the substituents, although they do vary with the addition pattern of the regioisomers. The device performance based on poly(3-hexylthiophene) (P3HT) and the fullerene bis-adduct regioisomer mixtures is enhanced by shortening the alkyl chain length. When using the regioisomerically separated fullerene bis-adducts, the devices based on <i>trans</i>-2 and a mixture of <i>trans</i>-4 and <i>e</i> of C4BA exhibit the highest power conversion efficiencies of ca. 2.4%, which are considerably higher than those of the C6BA counterparts (ca. 1.4%) and the C4BA regioisomer mixture (1.10%). There is no clear relationship between the PSC device performances and the LUMO energy levels of the fullerene regioisomers, whereas the film morphologies as well as electron mobilities of the P3HT:bis-adduct blend films are highly associated with the alkyl chain length of the substituents and the addition pattern of the regioisomers. Such structure–photovoltaic performance relationship provides valuable, basic information on the rational design of fullerene bis-adducts as an acceptor for highly efficient PSCs.</p> <p>In Chapter II, a pure <i>cis</i>-2 isomer of indene dimer-based fullerene bis-adduct has been synthesized, isolated and applied to bulk heterojunction solar cells for the first time. According to the work in Chapter I, PSCs based on the regioisomerically separated fullerene bis-adducts generally show superior device performances to those based on the corresponding regioisomer mixture. However, the mixture of <i>cis</i>-2 and <i>cis</i>-3 isomers is unable to be separated by</p>			

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<p>special HPLC method and even <i>cis</i>-1 is not generated due to the steric hindrance. As such, <i>cis</i>-isomers of fullerene bis-adducts have yet to be isolated for PSC applications, although the less steric hindrance of the <i>cis</i>-isomers would be favorable for their more close packing in the BHJ film and superior photovoltaic properties. In this chapter, synthesis and isolation of regioisomerically pure 1,2-bis(3-indenyl)ethane-(BIE)-C₆₀ adduct with <i>cis</i>-2 configuration, <i>cis</i>-2-BIEC, are achieved by the tether-directed functionalization method in moderate yield. The structure of <i>cis</i>-2-BIEC is fully characterized by ¹H and ¹³C-NMR spectroscopies, high-resolution mass spectrometry, UV-vis absorption spectroscopy and X-ray crystallography. <i>cis</i>-2-BIEC has a higher LUMO level as well as higher thermal stability than the mono-adduct mono-BIEC. In the PSC devices with P3HT as the donor, <i>cis</i>-2-BIEC shows a power conversion efficiency of 2.8% with the high V_{OC} of 0.80 V, outperforming the corresponding regioisomer mixture (bis-BIEC), BIE-C₆₀ adduct with one unreacted indene unit (mono-BIEC), and a widely used fullerene acceptor [60]PCBM. These results unambiguously demonstrate that <i>cis</i>-2 isomers of fullerene bis-adducts are highly potential candidates as an excellent electron-acceptor in PSC devices.</p> <p>In Chapter III, C₆₀ is replaced with C₇₀ aiming at increasing J_{SC} of PSC devices. An isomerically pure <i>cis</i>-2 C₇₀ bis-adduct, <i>cis</i>-2-[70]BIEC has been obtained for the first time through a similar method for the preparation of <i>cis</i>-2-[60]BIEC. The structure of <i>cis</i>-2-[70]BIEC is fully characterized by a series of analysis techniques including ¹H and ¹³C-NMR, high-resolution mass spectrometry, UV-vis absorption spectroscopy and X-ray crystallography. <i>cis</i>-2-[70]BIEC has two linking indenyl addends attached to α-bonds belonging to the same hemisphere, which is a unique addition pattern never reported before. A systematic study on the optical, electrochemical and photovoltaic properties of <i>cis</i>-2-[60]BIEC and <i>cis</i>-2-[70]BIEC as well as the corresponding mono-adducts has been performed to disclose the effects of the pure <i>cis</i>-2 regioisomers of C₆₀ and C₇₀. Molar absorption coefficients of <i>cis</i>-2-[70]BIEC and the corresponding mono-adduct α-mono-[70]BIEC between 400 nm to 700 nm are markedly increased in comparison with <i>cis</i>-2-[60]BIEC and mono-[60]BIEC. The LUMO energy level of <i>cis</i>-2-[70]BIEC is 0.10 eV higher than that of α-mono-[70]BIEC, but comparable to that of <i>cis</i>-2-[60]BIEC. The PSC based on <i>cis</i>-2-[70]BIEC and P3HT shows a remarkable power conversion efficiency of 4.2%, which is higher than those with <i>cis</i>-2-[60]BIEC (2.8%), α-mono-[70]BIEC (2.2%), and even a prevalent high-performance C₇₀ mono-adduct [70]PCBM (3.8%). These results suggest that the <i>cis</i>-2 isomer of C₇₀ bis-adducts is also a highly potential candidate as an excellent electron-acceptor in PSC devices. The synthetic strategy in this study paves the way for further development on the rational design and isolation of single fullerene bis-adduct regioisomers exhibiting high device performances.</p> <p>The last is a summary of this thesis. Overall, by utilizing a single fullerene bis-adduct isomer instead of the fullerene bis-adduct mixture, the V_{OC} and J_{SC} of PSCs have been improved concurrently. The V_{OC} is increased by the bis-functionalization of fullerenes, while the J_{SC} is enhanced by the isolation of the fullerene bis-adduct isomers. Further photovoltaic improvement will be realized by rational molecular design targeting at the smallest possible addend with a specific addition pattern on the fullerene.</p>			

(論文審査の結果の要旨)

本論文は、高効率太陽エネルギー変換の実現を目指して、ポリマー太陽電池用の新規電子アクセプターに着目したフラレン二付加異性体の合成と応用についてまとめたものである。得られた主な成果は以下の通りである。

1. フラレン C_{60} 二付加異性体の付加位置及び付加置換基構造が太陽電池特性に与える影響について検討した。混合物から各フラレン C_{60} 二付加異性体を分離・精製し、共役ポリマーとのバルク接合太陽電池を作製した結果、フラレン C_{60} 二付加異性体の付加位置及び付加置換基構造に太陽電池特性が大きく依存することを見いだした。また、共役ポリマーとの混合活性層構造がフラレン C_{60} 二付加異性体構造及び太陽電池特性と相関することを明らかにした。

2. 代表的な付加置換基であるインデンを短いスペーサーで架橋した 2 量体を設計し、フラレン C_{60} と反応させることで、特定の *cis*-2 型フラレン C_{60} 二付加異性体を選択的に合成することに初めて成功した。その結果、*cis*-2 型フラレン C_{60} 二付加異性体を用いたバルク接合太陽電池は代表的なフラレン C_{60} 誘導体 PCBM を用いた系と同程度の太陽電池特性を示すことを見いだした。

3. 本論文第三章で代表的な付加置換基であるインデンを短いスペーサーで架橋した 2 量体を設計し、フラレン C_{70} と反応させることで、特定の *cis*-2 型フラレン C_{70} 二付加異性体を選択的に合成することに初めて成功した。その結果、*cis*-2 型フラレン C_{70} 二付加異性体を用いたバルク接合太陽電池は代表的なフラレン C_{70} 誘導体 PCBM を用いた系を上回る太陽電池特性を示すことを見いだした。

以上、本論文は、ポリマー太陽電池性能を向上させるための電子アクセプターの合理的な分子設計と合成について述べており、学術上、實際上寄与するところが少なくない。よって、本論文は博士（工学）の学位論文として価値あるものと認める。また、平成 27 年 8 月 21 日、論文内容とそれに関連した事項について試問を行って、申請者が博士後期課程学位取得基準を満たしていることを確認し、合格と認めた。

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